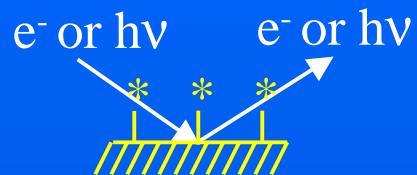


In-situ Monitoring of Heterogeneous Catalytic Reactions Using UV-Raman Spectroscopy: Bridging the Pressure and Material Gap

Craig R. Tewell
2001 ACS San Diego Conference
University of California at Berkeley
Department of Chemistry
April 2, 2001

Traditional Surface Science Approach

Before Reaction



UHV Characterization

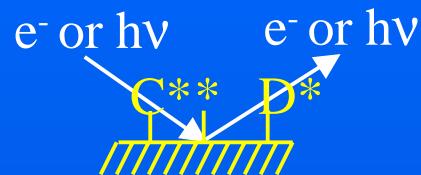
- * LEED - surface structure
- * AES - surface composition
- * XPS - surface composition & oxidation state
- * EELS - surface vibrational spectrum
- * TPD - heats of adsorption
- * ISS - surface composition

During Reaction

High P Monitoring

- * GC - gas composition

After Reaction

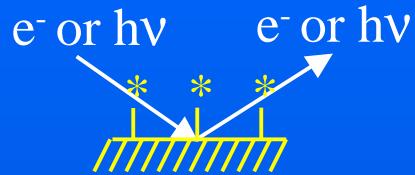


UHV Characterization

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- * AES - surface composition
- * XPS - surface composition & oxidation state
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Current Surface Science Approach

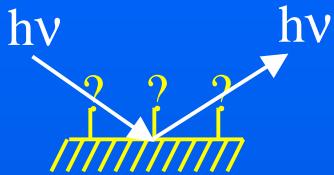
Before Reaction



Characterization

- * LEED - surface structure
- * AES - surface composition
- * XPS - surface composition & oxidation state
- * EELS - surface vibrational spectrum
- * TPD - heats of adsorption
- * ISS - surface composition
- * SFG - surface vibrational spectrum
- * Raman - vibrational spectrum

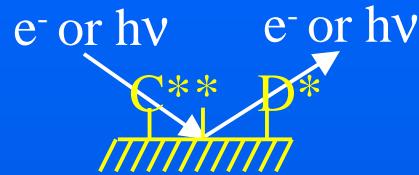
During Reaction



High P Monitoring

- * GC - gas composition
- * SFG - surface vibrational spectrum
- * Raman - vibrational spectrum

After Reaction

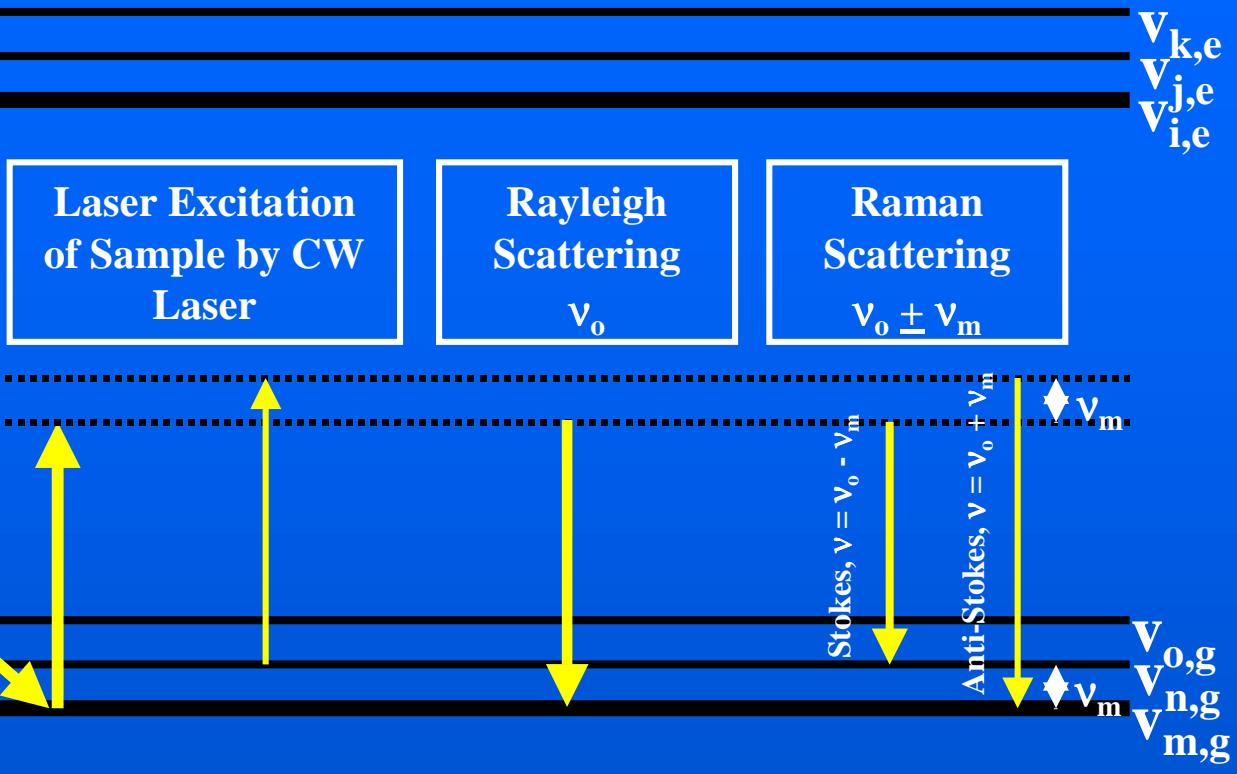


Characterization

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- * AES - surface composition
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- * SFG - surface vibrational spectrum
- * Raman - vibrational spectrum

Description of Normal Raman Scattering

1st Excited
Electronic State



$$I \propto I_o N \left(\tilde{v}_o - \tilde{v}_k \right)^4 |\alpha_{fg}|^2$$

$$\alpha_{fg} = \frac{1}{\hbar} \sum_r \left\{ \frac{\langle \Psi_f | P | \Psi_r \rangle \langle \Psi_r | P | \Psi_g \rangle}{\omega_{rf} + \omega_o} + \frac{\langle \Psi_f | P | \Psi_r \rangle \langle \Psi_r | P | \Psi_g \rangle}{\omega_{rg} - \omega_o} \right\}$$

Raman Shift vs Raman Photon

$$\text{Raman Shift, } \tilde{v}_m, \text{ cm}^{-1} = \tilde{v}_{\text{laser}} - \tilde{v}_k$$

Energy of excitation photon, cm^{-1}

$$\tilde{v}_{\text{laser}} = \frac{10^7}{\lambda_{\text{laser}}}$$

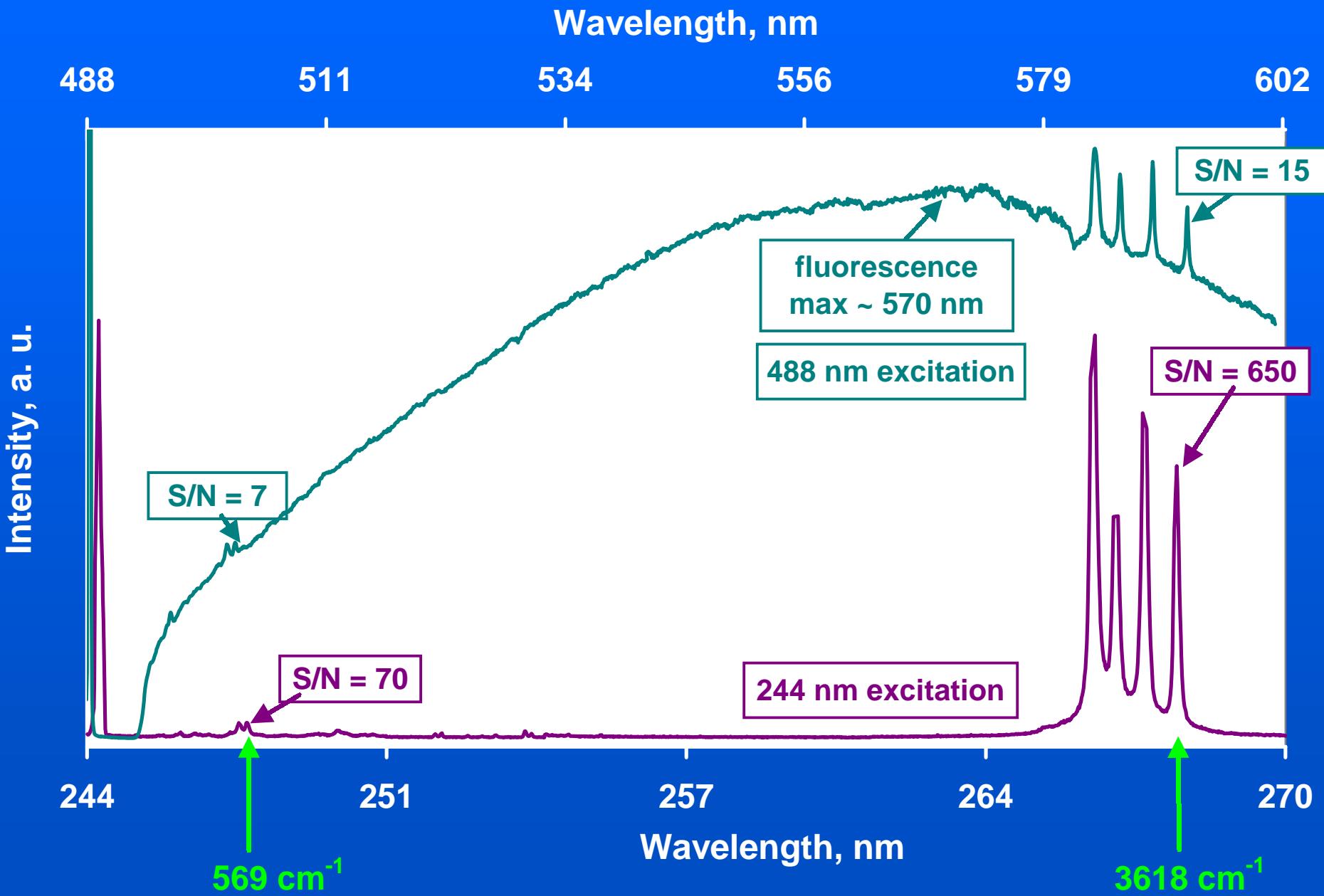
Energy of Raman photon, cm^{-1}

$$\tilde{v}_k = \frac{10^7}{\lambda_k}$$

$\lambda_{\text{laser}} = 488 \text{ nm}$				
Raman Shift	0 cm^{-1}	\rightarrow	λ_k	488 nm
Raman Shift	4000 cm^{-1}	\rightarrow	λ_k	606 nm

$\lambda_{\text{laser}} = 244 \text{ nm}$				
Raman Shift	0 cm^{-1}	\rightarrow	λ_k	244 nm
Raman Shift	4000 cm^{-1}	\rightarrow	λ_k	270 nm

Visible and UV Raman Spectrum of $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$



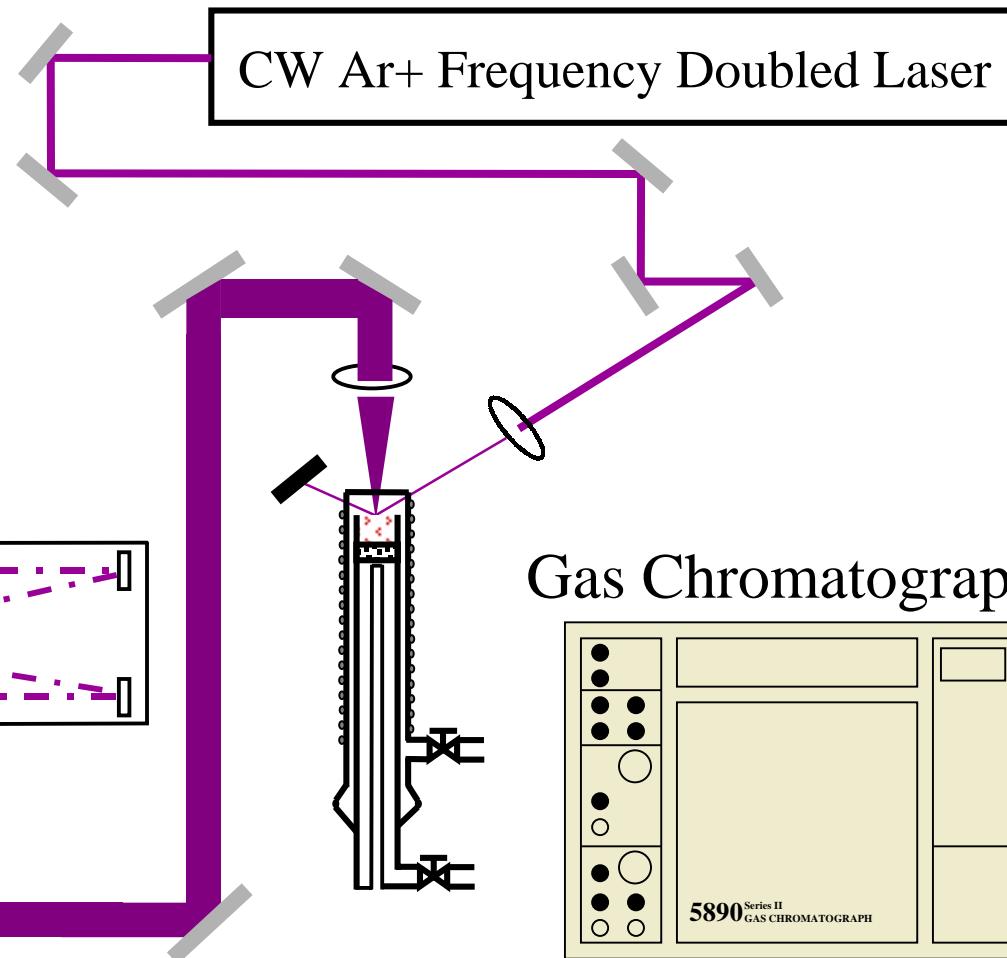
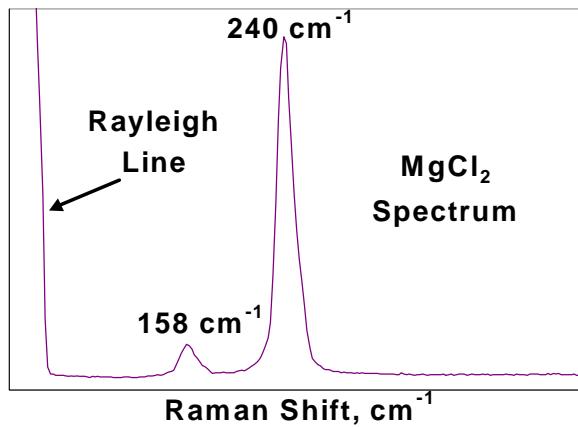
Why Raman Spectroscopy for Catalysis?

- routinely obtain spectrum from ~ 100 to 4000 cm^{-1}
- flexibility to choose frequency of excitation
 - avoid absorption of incident and scattered light
 - eliminate fluorescence interference
- detect changes in catalyst and adsorbed species
- obtain vibrational spectrum and kinetic information simultaneously under practical conditions

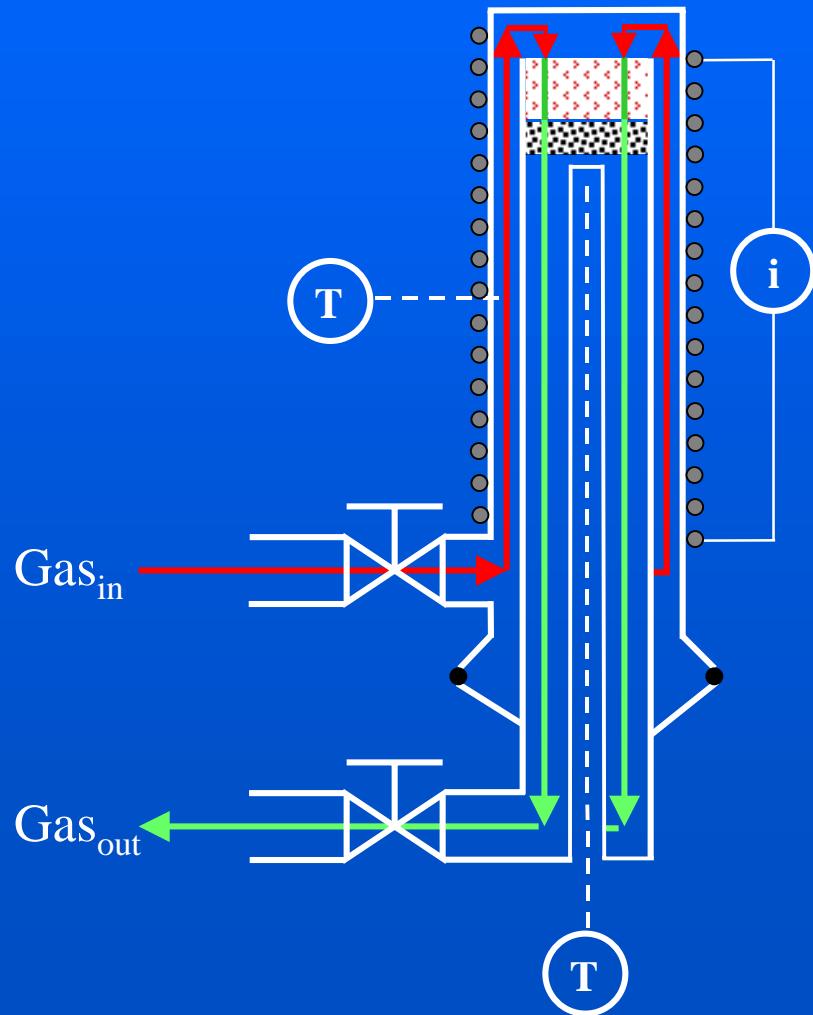
Reactor Design Criteria

- allow laser beam to probe the top of catalyst bed
 - fused silica window above catalyst bed
- avoid laser induced sample degradation
 - packed vs fluidized bed
- provide for reproducible feed/product GC sampling
 - 6-way GC valve
 - 8-way feed/product selection valve
- obtain quantitative kinetic information simultaneously under “practical” conditions

Experimental Setup



Packed Bed Reactor

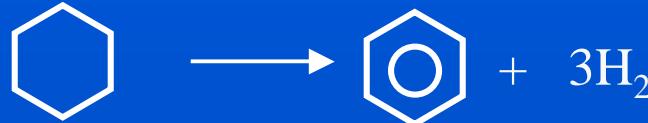


Advantages

- gas passes through catalyst bed
- fabricated from pyrex and quartz - no reaction with walls
- catalyst can be loaded in a dry box and kept in inert atmosphere
- 25 - 350°C operating range

Catalytic Naphtha Reforming

- petroleum refining process to increase octane number
- catalyst is Pt/ γ -Al₂O₃ or Pd-Pt/ γ -Al₂O₃ extrudates
- industrial operating conditions
 - Pressure Range: 3 - 24 atm
 - Temperature: 500-525°C
- desirable process chemistry

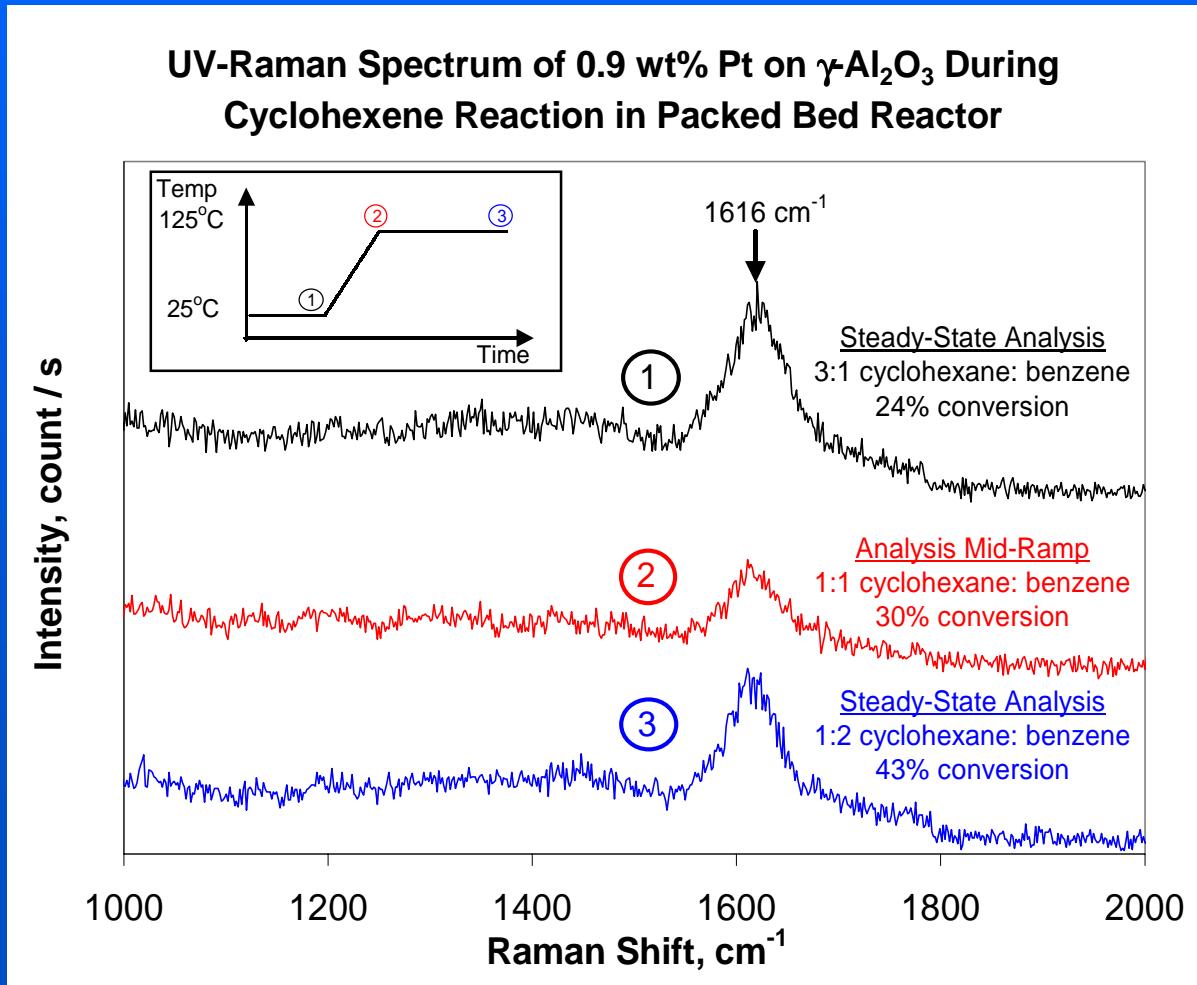


- undesirable process chemistry

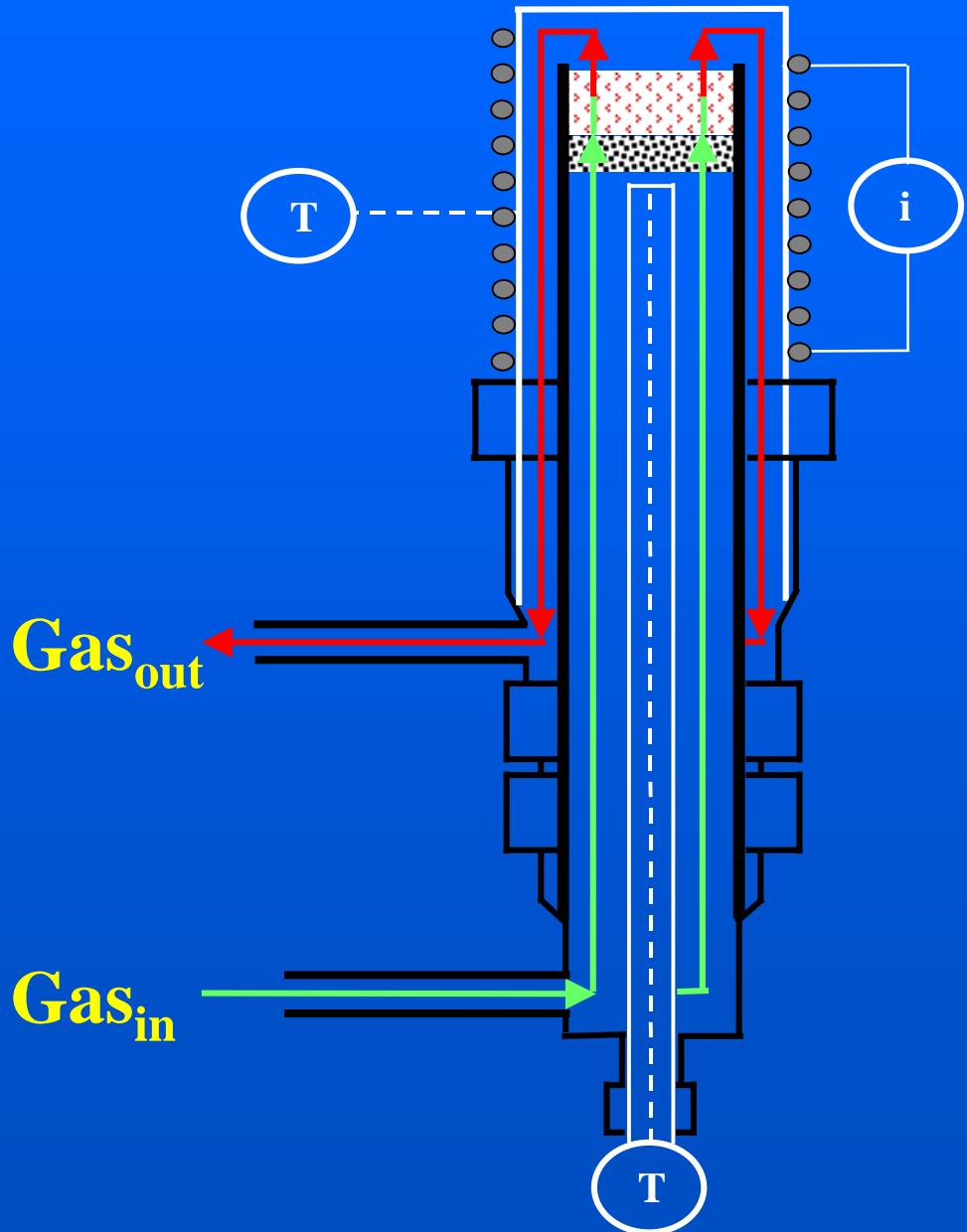


Preliminary Results

- cyclohexene reaction on 0.9 wt% Pt/ γ -Al₂O₃

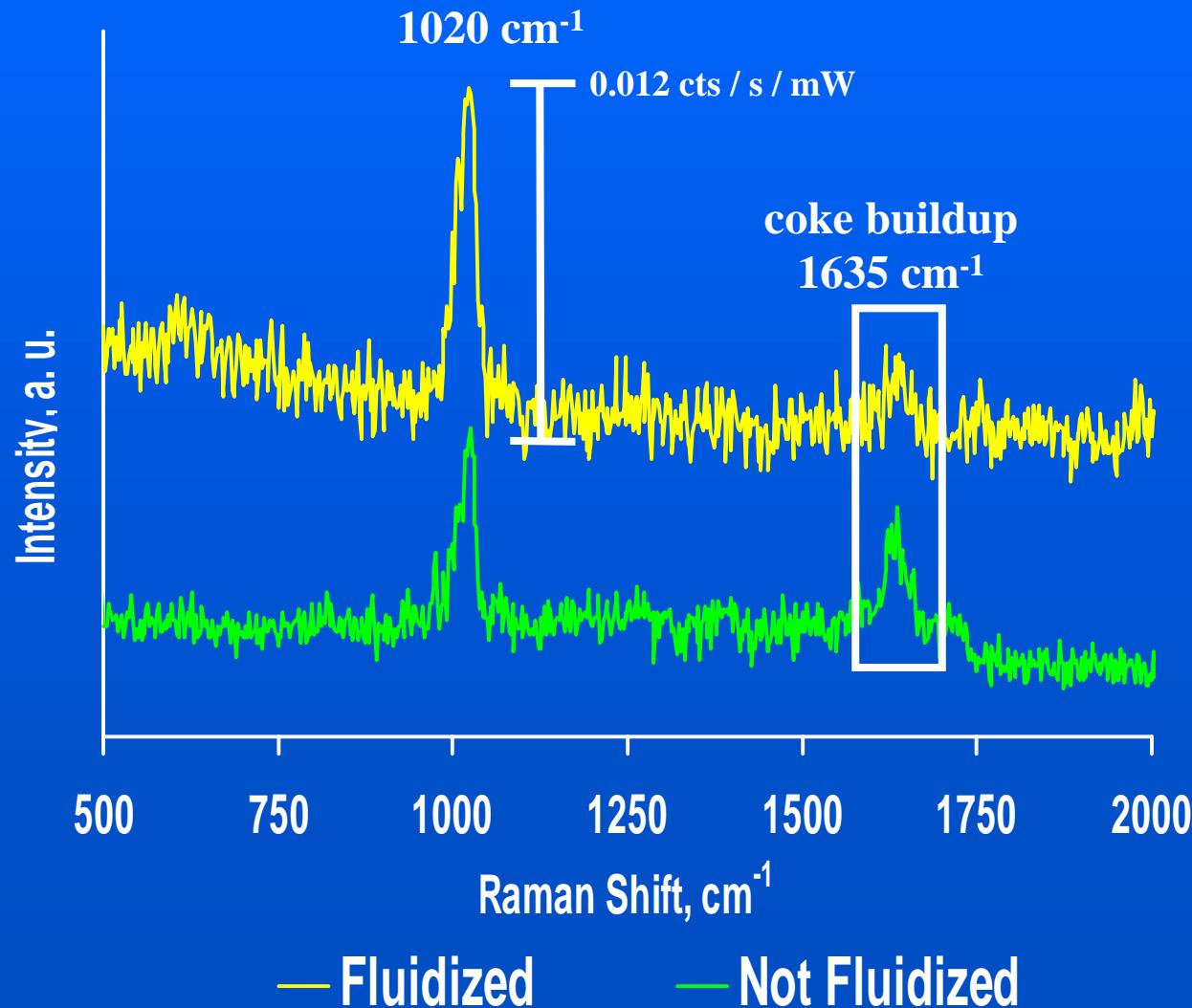


Fluidized Bed Reactor¹



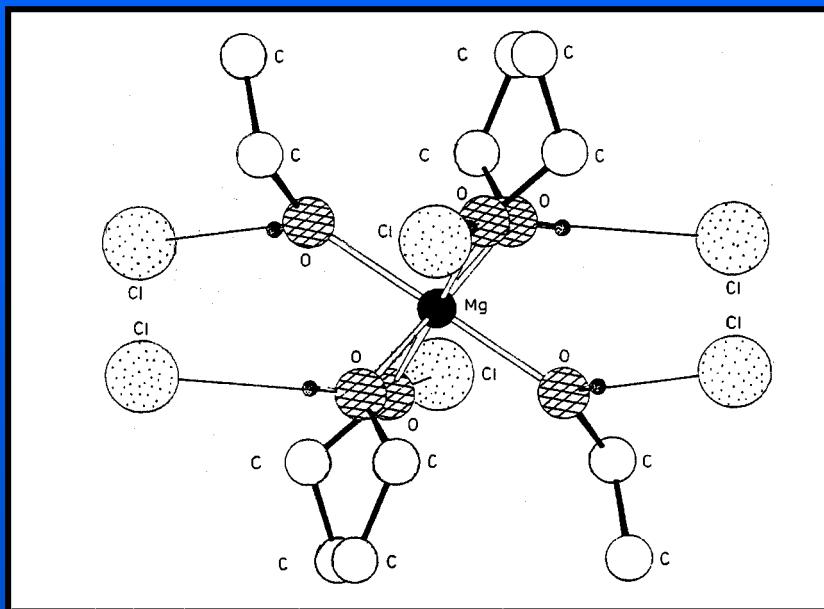
1. Design based upon the following reference: Chua, Y. T., Stair, P. C. "A Novel Fluidized Bed Technique for Measuring UV Raman Spectra of Catalysts and Adsorbates." *Journal of Catalysis* **196**: 66-72.

UV Raman Spectra of ZSM-5 with adsorbed pyridine

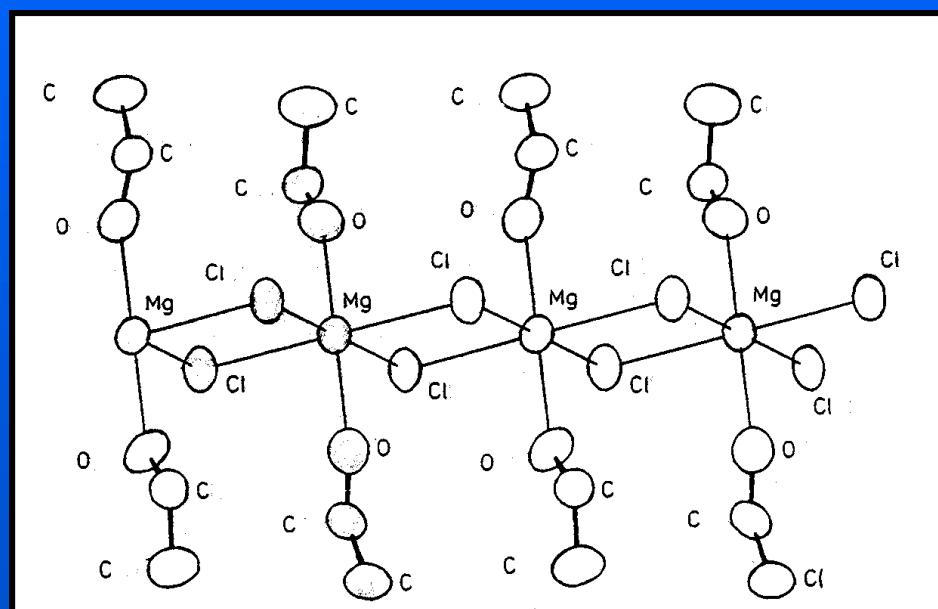


XRD Structure MgCl_2 -EtOH Adducts

$\text{MgCl}_2 - 6\text{EtOH}$

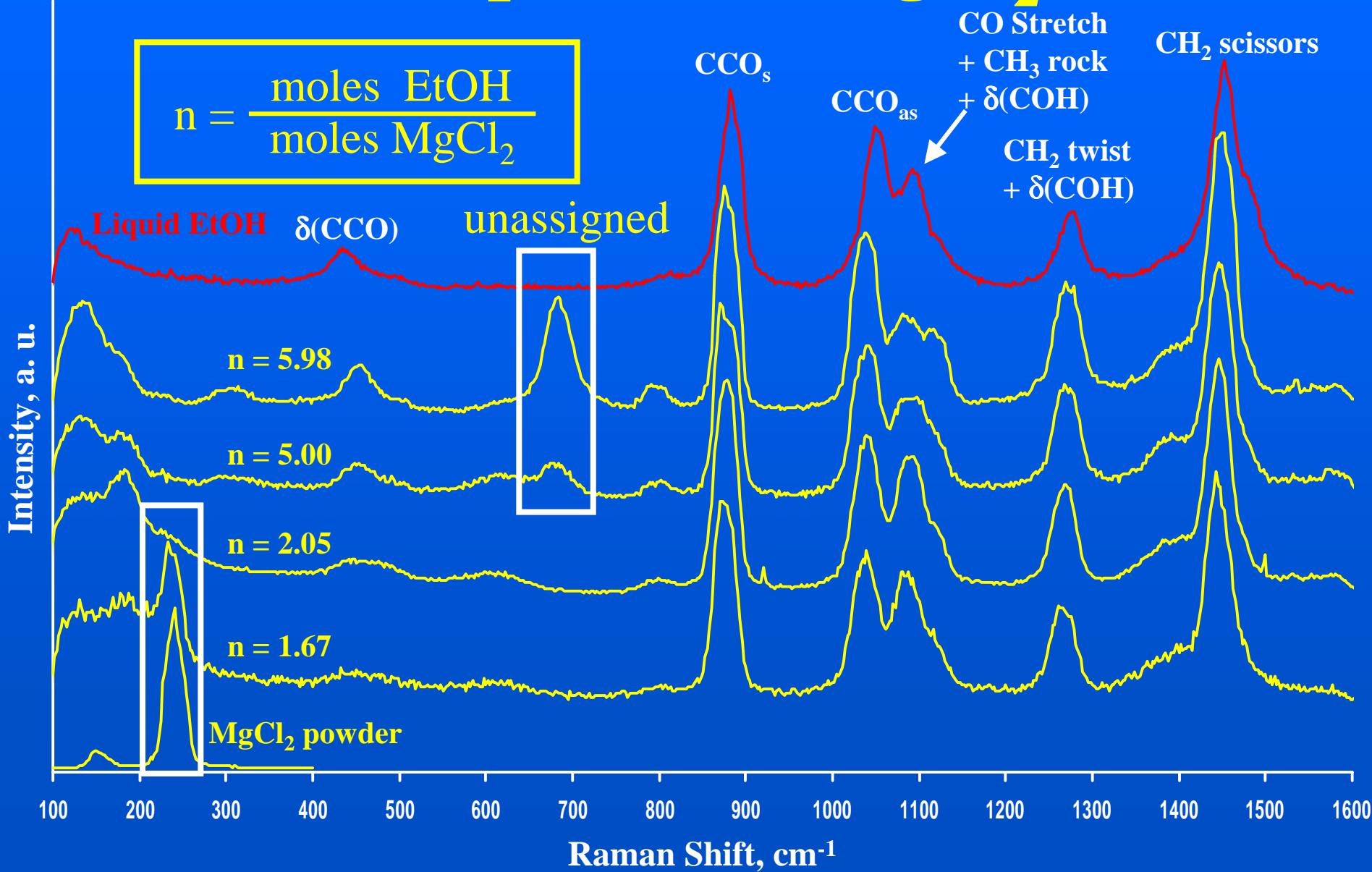


$\text{MgCl}_2 - 2\text{EtOH}$



Di Noto, Vito; Zannetti, Roberto; Viviani, Maria; Marega, Carla; Marigo, Antonio; Bresadola, Silvano. Makromol. Chem **193**: 1653-1663 (1992).

UV-Raman Spectra of MgCl_2 - nEtOH



UV-Raman Spectra of MgCl₂ - nEtOH

